

## Comment on “Low-Lying Quasiparticle States and Hidden Collective Charge Instabilities in Parent Cobaltate Superconductors”

Qian *et al*[1] recently reported angular-resolved photoemission spectroscopy (ARPES) measurements for  $\text{Na}_{0.8}\text{CoO}_2$  that show two concentric Fermi surfaces (FS) split by a  $\delta k_F$  that varies by a factor of three around the Brillouin zone (BZ). The surfaces occupy  $70 \pm 5\%$  of the full 2D BZ and were interpreted as the bonding and antibonding splitting (BAS) of the  $a_{1g}$  bands, with an unspecified effect of magnetic ordering. Below we show that this interpretation is not possible, and, in fact, no valid interpretation of the observed spectra in terms of the *bulk* electronic structure of  $\text{Na}_{0.8}\text{CoO}_2$  can be found.

The two formulas per unit cell of  $\text{Na}_x\text{CoO}_2$  double all bands in the Brillouin zone, including the observed  $a_{1g}$  band, formed by Co  $d_{z^2-1}$  orbitals. Symmetry mandates that the BAS is zero at  $k_z = \pi/c$ , but does not, in general, prescribe its  $k_z$  and  $k_{x,y}$  dependence. The crystal structure, however, only allows for sizeable hopping between Co planes via connecting O-O dumbbells. This fact and the  $d_{z^2-1}$  symmetry of the orbitals give rise to two corollaries: (a) the BAS is proportional to  $\cos k_z c$ , *i.e.*, maximal at  $k_z = 0$  and (b) the  $k_{x,y}$  dependence of the BAS is, to very good accuracy, proportional to  $t_{\text{O-O}}^2 \sum_i \cos \mathbf{A}_i \cdot \mathbf{k}_{xy}$ , where  $\mathbf{k}_{xy}$  is the in-plane vector and  $\mathbf{A}_{1,2,3}$  are the three nearest-neighbor Co-O vectors. Note that this functional form is not related to LDA or any other approximation (the value of the prefactor is), but only to the symmetry of the underlying Hamiltonian. At the edge of the first BZ this expression provides a maximum BAS angular anisotropy of  $\delta k_F / \langle \delta k_F \rangle < 15\%$  while at the  $k_F$  measured in Ref. 1  $\delta k_F / \langle \delta k_F \rangle < 2\%$ , to be compared with an observed factor of three. The discrepancy of three orders of magnitude leaves no doubt that the observed splitting is not the bulk BAS.

Contrary to a claim in Ref. 1, it is not the AFM ordering that “leads to canonical doubling of the unit cell”; it is doubled already without magnetism and the AFM only enhances the existing BAS. The total splitting is  $\sqrt{\tau^2 + \Delta_{ex}^2}$ , where  $\tau$  is the nonmagnetic BAS and  $\Delta_{ex}$  is the exchange splitting, which can, in principle, depend on  $\mathbf{k}_{xy}$ . However, this interpretation can also be safely excluded: doubly degenerate AFM FSs would contain 0.7 holes/formula, not 0.2, as required by Na content. Qian *et al* argue that “the 2D Luttinger count is not applicable to the FS of highly doped cobaltates”. However, for any practical purpose, it is: the cosine dependence of the BAS mandates that without AFM the Luttinger theorem (LT) is satisfied at each  $k_z$  *separately*. With AFM it is satisfied within  $\tau^2 / \Delta_{ex}^2$ , and to explain the large splitting anisotropy one has to assume that  $\tau \ll \Delta_{ex}$ .

Thus, the FS observed in Ref. 1 cannot represent the bulk FS. We now speculate on what kind of surface effects could help explain this observation. Since a polar surface cannot be stable[2], the termination layer in

$\text{Na}_x\text{CoO}_2$  cannot be  $\text{Na}_x$ , as in the bulk. Let it be  $\text{Na}_y$  ( $0 \leq y \leq x$ ). Conditions of nonpolarity and total neutrality imply that the top  $\text{CoO}_2$  layer then carries a charge of  $z = -(x/2 + y)$ , or  $1 - x/2 + y$  holes. The implicit assumption in Ref. 1 that the outermost  $\text{CoO}_2$  layer has the bulk hole concentration,  $\text{CoO}_2^{-x}$ , would require the surface Na concentration to be  $y = x/2$ . As we have argued, this assumption leads to a severe violation of the LT. Moreover, since the termination layer is now  $\text{Na}_{x/2}$ , the first and second  $\text{CoO}_2$  layers see different Na potentials. If ARPES were probing the top two  $\text{CoO}_2$  layers, two spin-split bands would be observed for each layer, totalling four bands for  $x = 0.8$ , (there is no known mechanism that would selectively suppress one spin, but not the other in non-spin-polarized PES), and two bands for  $x < 0.6$  (even in the absence of BAS and AFM). That neither is the case proves that only one  $\text{CoO}_2$  layer is probed.

For  $x = 0.8$ , the ARPES hole count is incompatible with  $\text{Na}_{x/2}$  termination. It is, however, approximately compatible with  $y = 0$  termination (no Na on the surface) where the top layer is  $\text{CoO}_2^{-0.4}$  (0.6 holes), roughly agreeing with  $0.70 \pm 0.05$ . The observed splitting may be ascribed to exchange, allowing at least for some possibility of explaining the angular anisotropy. Note that although the measured magnetic moment of  $0.13 \pm 0.02$  (at  $x = 0.82$ , Ref. 3) implies a larger FS splitting, the surface layer may be less polarized than the bulk. On the other hand, the *bulk* LT is fulfilled for the data in Fig. 2d of Ref. 1 for  $x \lesssim 0.6$ , compatible (assuming only the top layer is probed), with  $\text{Na}_{x/2}$  termination and a  $\text{CoO}_2^{-x}$  surface layer. While the electronic structure of this layer will not be identical to the bulk, its doping level is.

To summarize, we have shown that the observed[1] Fermi surfaces cannot represent the bulk electronic structure due to severe restrictions on the bonding-antibonding splitting anisotropy imposed by the crystal symmetry, and the impossibility of satisfying the LT, either with or without the AFM spin density wave. This conclusion is not model-specific and follows from general symmetry considerations. We also point out the impossibility of creating a nonpolar surface while maintaining the bulk Na concentration on the surface. The ARPES data of Ref. 1 appear to be fully understandable under the assumption that only the top  $\text{CoO}_2$  layer is probed, with a magnetically ordered surface with *no* Na termination for bulk doping  $x \gtrsim 0.6$ , and a nonmagnetic surface with *half* Na termination,  $\text{Na}_{x/2}$ , for  $x \lesssim 0.6$ [4]. The two observed FSs at  $x = 0.8$  then correspond to the two spin directions. We emphasize however, that these are only possible explanations and that the main purpose of our Comment is to show what *cannot* be rather than to speculate about what *can* be.

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- [1] D.Qian *et al*, Phys. Rev. Lett. **96**, 046407 (2006).  
[2] See discussion and further references in R. Hesper *et al*.  
Phys. Rev. B **62** , 16046 (2000).  
[3] S. P. Bayrakci *et al*, Phys. Rev. Lett. **94**, 157205 (2005)  
[4] Note that according to latest data  $x \approx 0.6$  separates the  
Pauli and Curie-Weiss regimes in magnetic susceptibility  
(H. Alloul, private communication).